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Office européen des brevets



(11) **EP 0 989 178 A1**

(12) **EUROPEAN PATENT APPLICATION**

published in accordance with Art. 158(3) EPC

(43) Date of publication:  
29.03.2000 Bulletin 2000/13

(21) Application number: 98919495.6

(22) Date of filing: 06.05.1998

(51) Int. Cl.<sup>7</sup>: **C10M 159/22**, C10M 169/04  
// (C10M169/04, 101:02,  
159:22), (C10N10/04, 20:00,  
20:02, 30:00, 30:04, 40:25)

(86) International application number:  
PCT/JP98/02012

(87) International publication number:  
WO 98/50500 (12.11.1998 Gazette 1998/45)

(84) Designated Contracting States:  
FR GB NL

(30) Priority: 07.05.1997 JP 13160397  
26.06.1997 JP 18462997  
26.03.1998 JP 9695498

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(54) **LUBE OIL COMPOSITION, OVERBASED ALKALINE EARTH METAL SULFIDE PHENEATE CONCENTRATE USED FOR PREPARING THE SAME, AND PROCESS FOR PREPARING THE CONCENTRATE**

(57) A lubricating oil composition having a high base value and an excellent high-temperature detergency and comprising an overbased alkaline earth metal phenate sulfide, and a process for producing an overbased alkaline earth metal phenate sulfide having a high base number and a viscosity at 100°C of 1,000 cSt or less and is excellent in hydrolytic stability and oil solubility. And, the overbased alkaline earth metal phenate sulfide concentrate is produced by introducing an alkaline earth metal reagent, a phenol compound in an amount of from 1 to 100 equivalents per mol of the alkaline earth metal reagent, and sulfur into a reactor optionally together with water; adding a dihydric alcohol

to the introduced mixture at a pressure inside the reactor of 10 to 250 kPa-G to react them; subsequently distilling off the excess dihydric alcohol and at least the excess amount of the water; treating the resultant bottom residue with carbon dioxide in the presence of from 0.3 to 0.8 mol of water per mol of the alkaline earth metal reagent; causing from 0.001 to 0.3 mol of a fatty acid compound to be present per mol of the alkaline earth metal reagent before the carbon dioxide treatment at the latest; and distilling off the excess phenol compound contained in the product of the carbon dioxide treatment.

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## Description

## TECHNICAL FIELD

[0001] The present invention relates to a novel overbased alkaline earth metal phenate sulfide concentrate useful as detergent dispersants for lubricating oils or fuel oils or as alkaline detergents, and to a process for producing the novel overbased alkaline earth metal phenate sulfide concentrate.

## BACKGROUND ART

[0002] Alkaline earth metal phenates are main additives for lubricating oils for internal combustion engines. Alkaline earth metal phenates serve to neutralize acidic substances generated mainly by combustion of a fuel in an internal combustion engine to thereby inhibit metal corrosion and lubricating oil deterioration and simultaneously accelerate dispersion of a sludge or a precursor therefor into the lubricating oil. Namely, the phenates are used for the purpose of inhibiting mechanical parts from sticking or wearing. Heat resistance, high-temperature cleaning ability, and oil solubility are important in the above application, and sulfurization of alkylphenols for improving these properties is known. A base number is an index of the ability to neutralize acids; the larger the value thereof, the higher the acid-neutralizing ability of the additive. In general, alkaline earth metal phenates in which the amount of the alkaline earth metal or alkaline earth metal ions is not less than 1/2 mol per mol of the alkylphenol are called "overbased" alkaline earth metal phenates.

[0003] Improvement of the base number is an important subject of study from the standpoint of improving the economy of the additives, and many reports have been made so far. For example, JP-W-1-501399 and JP-W-1-501400 have succeeded in obtaining a product having a base number exceeding 300 mg-KOH/g and a viscosity at 100°C of 1,000 cSt or less by incorporating into a phenate a carboxylic acid in an amount of from 2 to 40% by weight based on the whole and conducting a metal addition reaction at least one time. However, in these methods, in order to yield a product which simultaneously satisfies the two desirable properties, i.e., a high base number and a low viscosity, it has been necessary to conduct the metal addition reaction at least two times. According to the methods disclosed in JP-A-5-238976, JP-A-6-65192, and JP-A-6-184581, it is possible to improve the base number of an overbased alkaline earth metal phenate sulfide. However, this phenate sulfide has drawbacks of a dark hue and poor oil solubility. Although JP-W-1-501399 and JP-W-1-501400 propose addition of a fatty acid for improving the base number, those methods have a drawback that they necessitate a larger number of steps because the metal addition reaction should be conducted several times, leading to an increased production cost.

[0004] The present inventors previously proposed a method effective in eliminating the above problems in a process for producing an overbased alkaline earth metal phenate sulfide using an alkylphenol in an excess amount based on an alkaline earth metal reagent. In this method, the reaction mixture obtained after a metal addition and sulfurization reaction is distilled off to remove the excess dihydric alcohol and the water yielded by the reaction from the intermediate product and this intermediate product is then treated with carbon dioxide in the presence of a specific amount of water, in contrast to the conventional technique in which the water is regarded as a factor reducing phenate stability and is removed from the system. Furthermore, in the proposed method, a specific amount of a fatty acid compound is added before the carbon dioxide treatment. The present inventors thus succeeded in obtaining, through a metal addition reaction conducted only once, a product having a base number of from 250 to 400 mg-KOH/g and a viscosity at 100°C of 1,000 cSt or less. However, it has been still difficult to obtain a product having a base number exceeding 400 mg-KOH/g and a viscosity at 100°C of 1,000 cSt or less.

[0005] On the other hand, these products are required to have stability to water and water vapor because they are frequently used as lubricating oil additives for ship engines. Commercial alkaline earth metal phenate type additives are generally used as highly hydrolytically stable additives. However, when such additives are diluted to the same degree as in practical lubricating oils (base number: 30 mg-KOH/g) and this oil is tested according to the hydrolytic stability test method of ASTM D2619-88 without using a copper catalyst, then the base number retention after 24 hours is about 30% at the most.

[0006] As described above, no conventional alkaline earth metal phenates have been known which have a high base number and excellent hydrolytic stability.

[0007] It should be noted that the products which have conventionally been introduced as overbased alkaline earth metal phenates are products which in the present invention are referred to as overbased alkaline earth metal phenate sulfide concentrates (although some products have been introduced as overbased alkaline earth metal phenate sulfide concentrates). Namely, those products are overbased alkaline earth metal phenate sulfides in which the diluent which was used for synthesis is still contained in some degree. Because it is impossible to determine the exact structures of overbased alkaline earth metal phenate sulfides, the phenate sulfides have been defined by means of properties thereof in conventional patent documents, etc. However, this method has various problems.

[0008] For example, use of a base number for the definition of an overbased alkaline earth metal phenate sulfide has a problem that this base number value is not that of the overbased alkaline earth metal phenate sulfide but that of the overbased alkaline earth metal phenate sulfide concentrate. Consequently, even when two overbased alkaline earth metal phenate sulfides have the same base number (although there is no means for confirming it), they can be handled as products having different base numbers by regulating the amount of a diluent. Conversely, there have been cases where overbased alkaline earth metal phenate sulfide concentrates (or lubricating oil compositions) having the same base number differ in cleanness.

[0009] With respect to viscosity also, which, like a base number, is frequently used as a property of overbased alkaline earth metal phenate sulfides, it can be regulated by changing the amount of the diluent used.

[0010] Because definitions have conventionally been made by means of properties of not overbased alkaline earth metal phenate sulfides but overbased alkaline earth metal phenate sulfide concentrates as described above, no comparison has been made among overbased alkaline earth metal phenate sulfides themselves. There may hence be cases where overbased alkaline earth metal phenate sulfides which are virtually the same are judged to be different products or, conversely, different overbased alkaline earth metal phenate sulfides are judged to be the same product. Consequently, there has been a problem that correct judgements cannot be formed in investigations for obtaining an excellent overbased alkaline earth metal phenate sulfide.

[0011] An object of the present invention is to provide an overbased alkaline earth metal phenate sulfide concentrate which has a high base number and a viscosity at 100°C of 1,000 cSt or less, is excellent in hydrolytic stability and oil solubility, and is useful as a detergent dispersant for lubricating oils and the like and as an alkaline detergent, and to provide a process for producing the overbased alkaline earth metal phenate sulfide concentrate having a high base number and excellent in hydrolytic stability and oil solubility.

[0012] The present inventors made extensive studies in order to eliminate the above problems. As a result, it has surprisingly been found that the base number and hydrolytic stability of a product are considerably influenced by the amounts used of the starting materials and reaction ingredients, which should be within respective specific ranges, and by the sequence of introducing ingredients including a dihydric alcohol into the reactor and the reaction pressure in the step of introducing the dihydric alcohol into the reactor. The present invention has been completed based on these findings.

[0013] Furthermore, the present inventors have judged that a rational solution for the above-described problems cannot be expected if investigations are made based on the properties of overbased alkaline earth metal phenate sulfide concentrates as in conventional ones. The inventors have made intensive studies based on this judgement. As a result, they have found that even when lubricating oils are prepared so as to have the same base number, the lubricating oil having higher detergency at high temperatures is the one prepared with an overbased alkaline earth metal phenate sulfide concentrate which, upon extraction of the diluent, e.g., mineral oil, and neutral substances therefrom, gives a basic ingredient having a higher base number, and that higher cleanness can be imparted by using a lubricating base oil having a content of aromatic ingredients of from 1 to 10% by weight. The present invention has been completed based on these findings.

[0014] The term "overbased alkaline earth metal phenate sulfide concentrate" as used herein means not only a pure overbased alkaline earth metal phenate sulfide but also a product which has been diluted with a diluent, e.g., a mineral oil or the like. The term "basic ingredient" means the residue which is obtained by removing the diluent, e.g., mineral oil or the like, and neutral substances from an overbased alkaline earth metal phenate sulfide and is almost equal to the pure overbased alkaline earth metal phenate sulfide.

#### DISCLOSURE OF THE INVENTION

[0015] The present invention provides an overbased alkaline earth metal phenate sulfide concentrate having a base number of from 350 to 500 mg-KOH/g, a viscosity at 100°C of 1,000 cSt or less, and a fatty acid content of from 1 to 20% by weight based on the whole concentrate, wherein when the concentrate is diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the resultant dilution is hydrolyzed without adding a copper catalyst thereto by operation similar to the hydrolytic stability test method of ASTM D2619-88, a supernatant oil obtained by centrifuging the sample after 24 hours has a base number retention of 70% or more.

[0016] Furthermore, the present invention provides a process for producing the overbased alkaline earth metal phenate sulfide concentrate, comprising introducing an alkaline earth metal oxide, an alkaline earth metal hydroxide or a mixture thereof (hereinafter referred to as an "alkaline earth metal reagent"), a phenol compound in an amount of from 1 to 100 equivalents per mol of the alkaline earth metal reagent, and sulfur into a reactor optionally together with water; adding a dihydric alcohol to the introduced mixture at a pressure inside the reactor at 10 to 250 kPa-G to react them; subsequently distilling off the excess dihydric alcohol and at least the excess amount of the water; treating the resultant bottom residue with carbon dioxide in the presence of from 0.3 to 0.8 mol of water per mol of the alkaline earth metal reagent; causing from 0.001 to 0.3 mol of a fatty acid compound to be present per mol of the alkaline earth metal reagent.

gent before the carbon dioxide treatment at the latest; and distilling off the excess phenol compound contained in the product of the carbon dioxide treatment.

[0017] Moreover, the present invention furthermore provides a lubricating oil composition having a base number of from 10 to 200 mg-KOH/g, comprising: the above overbased alkaline earth metal phenate sulfide concentrate containing an overbased alkaline earth metal phenate sulfide having a base number of from 550 to 700 mg-KOH/g; and a lubricating base oil having a content of aromatic ingredients of from 1 to 10% by weight.

#### BRIEF DESCRIPTION OF THE DRAWING

[0018]

Fig. 1 is a diagrammatic view illustrating an example of a rubber film extraction apparatus. Numeral 1 denotes a water bath, 2 a flask, 3 a thermometer, 4 a sample oil, 5 a rubber film, 6 a thimble paper filter, 7 fixing with a thread, 8 a glass bulb, 9 a condenser, and 10 water.

#### BEST MODES FOR CARRYING OUT THE INVENTION

[0019] Examples of the phenol compound for use in the present invention include phenols having a hydrocarbon side chain, for example, having from 4 to 36 carbon atoms, preferably from 8 to 32 carbon atoms, e.g., an alkyl group, an alkenyl group, or an aralkyl group. Specific examples of these phenol compounds include phenols having a hydrocarbon group, such as butyl, amyl, octyl, nonyl, dodecyl, cetyl, ethylhexyl, triacontyl, or the like, or having a group derived from a petroleum hydrocarbon, such as a liquid paraffin, wax, or an olefin polymer (e.g., polyethylene, polypropylene, polybutene, or the like). These phenol compounds are used alone or as a mixture of two or more thereof. It is preferred to use a phenol compound which becomes aqueous at temperatures of generally about 130°C or less, preferably about 120°C or less.

[0020] The alkaline earth metal reagent to be used is generally an oxide or hydroxide of an alkaline earth metal or a mixture of these. For example, the oxide or hydroxide of calcium, barium, strontium, magnesium, or the like is used. The amount used of the phenol compound is from 1 to 100 equivalents, preferably from 1.6 to 10 equivalents, per mol of the alkaline earth metal reagent. If the amount of the phenol compound relative to that of the alkaline earth metal reagent is too small, an intermediate gels and does not react any more, so that the target satisfactory product cannot be obtained. On the other hand, too large amounts of the phenol compound relative to the amount of the alkaline earth metal reagent not only result in a reduced yield of the product based on the starting materials, but also are economically disadvantageous because recovery of the phenol compound necessitates much utility cost and time.

[0021] Next, the dihydric alcohol to be used is one having a relatively low boiling point, a low viscosity, and a high reactivity. The dihydric alcohol preferably has from 2 to 6 carbon atoms. Especially, ethylene glycol, propylene glycol, and the like are preferred. The dihydric alcohol accelerates the conversion of the alkaline earth metal reagent into an oil-soluble substance through reaction with the phenol compound, stabilizes the oil-soluble intermediate, and is partly incorporated into the phenate product to constitute a polyvalent phenate. In the process of the present invention, the metal addition reaction may be conducted in the presence or absence of water, which has a reaction-accelerating effect. In the case of conducting the reaction in the presence of water, the amount used of the dihydric alcohol is preferably about from 0.15 to 3.0 mol, especially about from 0.3 to 1.5 mol, per mol of the alkaline earth metal reagent. In the case of conducting the reaction in the absence of water, the amount used of the dihydric alcohol is preferably about from 1.0 to 3.0 mol, especially about from 1.2 to 2.0 mol, per mol of the alkaline earth metal reagent. If the amount used of the dihydric alcohol is too small, the conversion of the starting materials, especially of the alkaline earth metal reagent, into the product is reduced. If the amount thereof is too large, distillation for removing the excess dihydric alcohol from the reaction product necessitates much time and utility cost, although the metal addition reaction of the phenol compound proceeds smoothly.

[0022] Sulfur is used in an amount of from 0.001 to 3.0 mol, preferably from 0.01 to 0.5 mol, and more preferably from 0.05 to 0.4 mol, per mol of the alkaline earth metal reagent. As the amount used of sulfur is reduced, the viscosity of the product decreases. However, if the sulfur amount is too large, the resultant product is less overbased and a product having a high base number is hence difficult to obtain. In addition, the product viscosity is exceedingly high. Thus, the target product having a low viscosity and a high base number cannot be obtained.

[0023] In the case where water is added to the reaction system for the purpose of accelerating the reaction in the step of a metal addition reaction in which the phenol compound is allowed to react with the alkaline earth metal reagent, use can be made of brackish water, industrial water, the water yielded by the metal addition reaction, or the like, as well as distilled water, without particular limitations on the quality thereof. Water of any state, e.g., cold water, warm water, steam, or the like, can be used. The water to be used for accelerating the metal addition reaction may be introduced alone into the reactor. Alternatively, part or all of the water may be added as a mixture with a starting material such as

the phenol compound or the dihydric alcohol. The time when water is introduced into the reactor is not particularly limited and may be either before or after the mixing of all starting materials other than water. It is, however, preferred to add water within about 1 hour after the mixing of all starting materials.

[0024] The amount of the water added to the reaction system in order to accelerate the metal addition reaction is about from 0.01 to 10 mol, preferably from 0.1 to 2.0 mol, per mol of the alkaline earth metal reagent used. When the metal addition reaction is conducted in the presence of water externally added to the reaction system, the reaction proceeds more smoothly than in the case where the reaction is conducted under the same conditions except that water is not added. As a result, the conversion of the starting materials, especially of the alkaline earth metal reagent, into the product is high. Consequently, if the amount of the water added to the reaction system is too small, the conversion of the alkaline earth metal reagent into the product is reduced. Conversely, if the amount thereof is too large, the advantage that the distillation step after reaction is simplified is lost.

[0025] The water to be present during the carbon dioxide treatment is generally added after the starting material mixture comprising a phenol compound, a dihydric alcohol, an alkaline earth metal reagent, and sulfur and optionally further containing water is allowed to react to complete a metal sulfide addition reaction and the resultant reaction mixture is distilled off to remove the water and the excess dihydric alcohol. The water to be present during the carbon dioxide treatment is not particularly limited in its quality and conditions like the water used for accelerating the metal addition. The amount of water in the reaction system is adjusted to from 0.3 to 0.8 mol, preferably from 0.3 to 0.6 mol, per mol of the alkaline earth metal reagent. In the case where the dihydric alcohol is present in excess in the system, all water present in the system, including the water added first and the water yielded by the reaction, goes away as an initial fraction during distillation for removing the dihydric alcohol. It is, therefore, necessary to add a given amount of water after the excess dihydric alcohol has been distilled off. On the other hand, in the case where no excess dihydric alcohol is present in the system, the water present in the system after completion of the metal sulfide addition reaction, including the water added before the reaction for accelerating the same and the water yielded by the reaction, may be partly removed so that only the excess amount thereof is distilled off to leave a given amount of water. However, if the amount of the residual water is unclear, it is preferred to distill off all water and then add a given amount of water. As the amount of the water present during the carbon dioxide treatment increases, the base number of the product is improved. However, too large water amounts result in excessive hydrolysis of the product and this causes a decrease in the base number and oil solubility. If the water amount is too small, the effect of improving the product base number cannot be obtained sufficiently.

[0026] The fatty acid compound which is caused to be present before the carbon dioxide treatment is a fatty acid, for example, having from 10 to 30, preferably from 16 to 24, carbon atoms or a salt thereof. The salt is preferably an alkaline earth metal salt. Examples of the alkaline earth metal include calcium, barium, magnesium, strontium, and the like. The fatty acid compound is more preferably one in which the alkyl group is linear. Specific examples of the fatty acid compound include decanoic acid, capric acid, lauric acid, palmitic acid, stearic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid, and the like. Stearic acid is preferred. The fatty acid compound may be a mixture having a molecular weight distribution, and a commercial stearic acid product having a stearic acid purity of about from 60 to 70% can be used. The amount of the fatty acid compound is from 0.001 to 0.3 mol, preferably from 0.01 to 0.3 mol, more preferably from 0.05 to 0.3 mol, and most preferably from 0.05 to 0.2 mol, per mol of the alkaline earth metal reagent. If the amount of the fatty acid compound added is too small, no further improvement in the phenate base number is observed and the phenate concentrate obtained has an impaired hue and reduced oil solubility. If the amount thereof is too large, the resultant phenate concentrate has a reduced base number.

[0027] In the present invention, a diluent or solvent having an appropriate viscosity (hereinafter referred to as a "diluent") can be added in order to facilitate the handling of reactants or of the intermediate, product, or the like. For example, the recovery of the unreacted phenol compound by distillation from the reaction product resulting from the metal addition reaction step or carbon dioxide treatment can be conducted in the presence of a diluent having a high boiling point and an appropriate viscosity, whereby a bottom residue in a desirable liquid state can be obtained. In general, a part of the diluent is distilled off by being accompanied with the distillation of the unreacted phenol compound. It is therefore preferred to use a diluent which does not exert a direct adverse influence on the reaction, in the case where the phenol compound recovered is recycled to the reaction. It is also possible to conduct the reaction in the presence of a diluent. Preferred examples of the diluent include petroleum fractions having an appropriate viscosity, such as paraffinic, naphthenic, or aromatic base oils and mixtures thereof, and the like, specifically, lubricating oil fractions having a boiling point of about from 220 to 550°C and a viscosity at 100°C of about from 2 to 40 cSt. Other organic solvents also can be used as diluents as long as they are hydrophobic and lipophilic and are harmless for both the reaction and applications of the product. For example, higher alcohols having from 8 to 24 carbon atoms can be used.

[0028] In a process for producing the overbased alkaline earth metal phenate sulfide concentrate of the present invention, an alkaline earth metal reagent, a phenol compound, and sulfur are first introduced into a reactor optionally together with water and these ingredients are mixed together. A fatty acid compound may be fed together with these ingredients. The order of feeding these starting materials and reaction ingredient is not particularly limited, and may be

suitably selected.

[0029] A dihydric alcohol can be added to the introduced mixture at a pressure inside the reactor at 0 to 250 kPa-G. For obtaining an overbased alkaline earth metal phenate sulfide concentrate having the sufficient properties described herein, the addition of a dihydric alcohol is conducted preferably at a pressure of from 10 to 250 kPa-G, especially from 20 to 230 kPa-G. By adding a dihydric alcohol to the introduced mixture at a pressure within that range, an overbased alkaline earth metal phenate sulfide concentrate having a high base number and excellent hydrolytic stability can be produced. Although the addition of the dihydric alcohol is conducted when the pressure inside the reactor is within the above range, 60% by weight or more, preferably 80% by weight or more, of the whole dihydric alcohol is preferably added at a pressure within that range.

[0030] At the time when a dihydric alcohol is added, the temperature of the mixture introduced is preferably 60°C or more, especially 120°C or more. The upper limit of temperature of the introduced mixture at the time of dihydric-alcohol addition is generally lower than the boiling point of the introduced mixture, and is preferably 200°C or less.

[0031] The dihydric alcohol to be added is preferably heated beforehand to a temperature within that range.

[0032] The dihydric alcohol is generally added over 20 to 90 minutes, preferably 30 to 60 minutes.

[0033] After completion of the addition of the dihydric alcohol, the resultant mixture is allowed to react at a temperature within the range of about from 60 to 200°C, preferably about from 90 to 190°C. The pressure is not particularly limited, and is selected in the range of from 0.01 to 21 atm · A, preferably from 0.1 to 11 atm · A. The unit "atm · A" means an absolute pressure; 1 atm · A corresponds to 0 atm · G, i.e., 101.3 kPa. This reaction almost terminates usually in a period of from 1 to 9 hours.

[0034] The step of the carbon dioxide treatment is conducted in the following manner. After completion of the metal addition reaction, the excess dihydric alcohol compound present in the system and at least the excess amount of the water are distilled off. In the case where a fatty acid compound is not initially added or is initially added in a small amount, a fatty acid compound is added so as to result in a given amount. Furthermore, a given amount of water is caused to be present in the system. Thereafter, the resultant mixture is allowed to react with carbon dioxide under conditions of a reaction temperature of about from 50 to 230°C, preferably from 80 to 200°C. This reaction may be conducted at any one of reduced, ordinary, and elevated pressures. In general, a pressure of from 0.01 to 51 atm · A, preferably from 0.1 to 31 atm · A, is employed. The reaction is generally conducted until the absorption of carbon dioxide terminates, which takes from 20 minutes to 10 hours, usually from 20 minutes to 3 hours. If necessary, the product thus obtained is held in a carbon dioxide atmosphere at about from 100 to 230°C and a pressure of from 0 to 20 atm · G, preferably from 0 to 10 atm · G, for from several minutes to several ten hours. Through the carbon dioxide treatment, the product is further improved in performances required for lubricating oil additives and fuel oil additives, especially in solubility in engine oils and stability therein.

[0035] The fatty acid compound may be added at any time after introduction of starting materials into the reactor and before the step of the carbon dioxide treatment, preferably before the addition of water for the carbon dioxide treatment. It is also possible to further conduct metal addition by adding an alkaline earth metal reagent and a dihydric alcohol, optionally together with a fatty acid compound, to the reaction product resulting from the carbon dioxide treatment and conducting the same metal addition reaction as the above, followed by carbon dioxide treatment at least one time. From the standpoints of profitability, etc., the unreacted phenol compound remaining in the reaction product after the carbon dioxide treatment is preferably recovered partly or mostly. The recovered phenol compound can be reused as a starting material. When the distillation for recovering the unreacted phenol compound is conducted in the presence of an ordinary diluent, e.g., a high-boiling mineral oil, a distillation residue can be obtained in a preferred liquid state. The insoluble substances contained in the distillation residue can be removed by filtration, centrifuging, or another means before or after the recovery of the phenol compound.

[0036] The overbased alkaline earth metal phenate sulfide concentrate of the present invention has a base number of from 350 to 500 mg-KOH/g, preferably from 400 to 500 mg-KOH/g, a viscosity at 100°C of 1,000 cSt or less, preferably from 100 to 1,000 cSt, and a fatty acid compound content of from 1 to 20% by weight, preferably from 5 to 15% by weight, based on the whole concentrate. The values of viscosity were determined by the test method according to JIS K-2283 with a Zeitfuchs cross-arm viscometer.

[0037] When the overbased alkaline earth metal phenate sulfide concentrate of the present invention is diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the resultant dilution is contacted at 93°C for 24 hours with 5 wt% water based on the total amount, then the base number retention after the treatment is 70% or more, preferably 80% or more, and especially preferably 90% or more.

[0038] The overbased alkaline earth metal phenate sulfide concentrate of the present invention has the properties described above. Because of these properties, it has a high base number and is excellent in hydrolytic stability and oil solubility.

[0039] The overbased alkaline earth metal phenate sulfide concentrate of the present invention is obtained by reacting a phenol compound, a dihydric alcohol, an oxide of an alkaline earth metal, a hydroxide of an alkaline earth metal or a mixture thereof (hereinafter referred to as an "alkaline earth metal reagent"), and sulfur. However, the concentrate

is especially preferably one obtained by the above-described process of the present invention for producing an overbased alkaline earth metal phenate sulfide concentrate.

[0040] The process of the present invention for producing an overbased alkaline earth metal phenate sulfide is intended not to yield an overbased alkaline earth metal phenate sulfide concentrate containing a basic ingredient in a heightened concentration but to yield an overbased alkaline earth metal phenate sulfide concentrate in which the basic ingredient has a heightened base number.

[0041] The overbased alkaline earth metal phenate sulfide obtained by the process described above can be used as a detergent for lubricating oils or fuel oils or as an alkaline detergent.

[0042] The base oil ingredient for use in the lubricating oil composition of the present invention is a lubricating base oil having a content of aromatic ingredients of from 1 to 10% by weight. The content of aromatic ingredients in the lubricating base oil is preferably from 1 to 7% by weight, especially preferably from 2 to 5% by weight.

[0043] Preferred examples of the lubricating base oil having a content of aromatic ingredients of from 1 to 10% by weight include lubricating base oils purified by solvent dewaxing and lubricating base oils purified by cryogenic dewaxing. With respect to base oils purified by hydrogenation dewaxing, those in which the content of aromatic ingredients is less than 1% by weight are undesirable. Such base oils may be used alone or as a mixture of two or more thereof. A lubricating base oil which has been mixed with a synthetic base oil may also be used so long as the content of aromatic ingredients in the mixture is from 1 to 10% by weight.

[0044] In the lubricating oil composition of the present invention, the proportion of the overbased alkaline earth metal phenate sulfide having a base number of from 550 to 700 mg-KOH/g to the lubricating base oil having a content of aromatic ingredients of from 1 to 10% by weight may be such that the lubricating oil composition obtained has a base number of usually in the range of from 10 to 200 mg-KOH/g.

[0045] The lubricating oil composition of the present invention preferably has a cleanliness score of 5.5 or more, especially 6.0 or more, according to a hot-tube test.

[0046] The lubricating oil composition of the present invention can be used in various parts where lubrication is necessary.

#### EXAMPLES

[0047] The present invention will be explained below in more detail by reference to Examples, which are mere examples, and should not be construed as limiting the present invention.

[0048] The rubber film extraction method, the hot-tube test, and the determination of aromatic ingredients in lubricating base oils conducted in the Examples are shown below.

##### (1) Rubber Film Extraction Method

[0049] Rubber film extraction was conducted in the following manner. A thimble paper filter having a diameter of 60 mm and a length of 200 mm (Type 21500-05, manufactured by Ogura Glass Kogyo K.K.) was set in a Soxhlet's extractor made of glass (Type 21300-01, manufactured by Ogura Glass Kogyo K.K.) as shown in Fig. 1. In a rubber film bag (Skinless Skin Crown, Thin Type, Almighty; manufactured by Okamoto Industries, Inc.; washed with hexane prior to use), 20 g of a sample was placed. This rubber film bag was attached to the glass bulb and fastened with a thread. This structure was set in the cylindrical filter paper. In the flask, 700 ml of hexane was placed. Extraction was conducted for 15 hours under heating and refluxing the hexane in an 85°C water bath.

##### (2) Hot-tube Test

[0050] The hot-tube test is a cleanliness test method common to the person skilled in the art.

[0051] Hot-tube tester HT-201 Type, manufactured by Komatsu Setsubi K.K., was used. A glass tube (inner diameter: 2 mm; length: 300 mm) through which air was passed at a rate of 10 ml/min was heated to 300°C, and a sample oil was passed therethrough at a rate of 0.31 ml/hr. The color of the sample after 16 hours was compared with that in a standard test, and rated on the maximum of 10 points.

[0052] The hot-tube tests respectively for the Examples and Comparative Examples were conducted simultaneously in order to diminish the experimental error. Each sample was tested twice and the results were averaged.

##### (3) Determination of Aromatic Ingredients in Lubricating Base Oil

[0053] The aromatic ingredients contained in a lubricating base oil were determined according to "Chromatographic Rapid Microanalysis of Lubricating Oil" described in Wataru Funasaka, ed., *Nenryo Bunseki Shikensho (Test Methods for Fuel Analysis)*, Nankodo, p. 391. The determination was made on a 4-fold scale using adsorbent No. 7734 (70-230



mesh), manufactured by Merck & Co., Inc. in the following manner. A chromatographic glass tube packed with 40 g of silica gel which had been dried and activated at 160°C for 8 hours was used. Two grams of a lubricating base oil was precisely weighed out, diluted with 40 ml of a petroleum ether, and then injected into the chromatographic tube. The operation of elution with a petroleum ether was conducted until the elution of oil ingredients came not to occur any more, and the saturated solvent was recovered. Subsequently, aromatic ingredients were eluted with diethyl ether. With respect to each of the two fractions, the solvent was removed with a rotary evaporator at 30°C and a reduced pressure of about 30 mmHg, and the residue was weighed.

#### EXAMPLE 1

[0054] Into a 1-liter autoclave equipped with a stirrer, gas introduction tube, and thermometer, 531.2 g (1.9 mol) of dodecylphenol having a purity of 97.9%, 40.91 g (0.7 mol) of calcium oxide having a purity of 96.0%, 3.37 g (0.105 mol) (0.15 mol per mol of the calcium oxide) of sulfur, and 25.2 g (0.091 mol) (0.13 mol per mol of the calcium oxide) of stearic acid were introduced. The autoclave was sealed and the contents were stirred. The resultant suspension was heated to 125°C. To this suspension, 65.21 g (1.05 mol) of ethylene glycol having a purity of 94.5% was added over 30 minutes at 125°C and a pressure of about 60 kPa-G. This mixture was stirred for about 3.0 hours in the closed vessel at 130°C and an elevated pressure of about 500 kPa-G. Thereafter, the water yielded, part of the unreacted ethylene glycol, and a small proportion of the dodecylphenol were distilled off while gradually reducing the pressure of the reaction system. As a result, 791.9 g of a liquid distillation residue was obtained. In this distillation, the final distillation temperature was 141°C (5 mmHg). Subsequently, 5.67 g (0.32 mol) (0.45 mol per mol of the calcium oxide) of water was added to 791.9 g of the distillation residue, and the resultant mixture held in a reduced-pressure atmosphere was caused to absorb carbon dioxide at a temperature of 150°C for 30 minutes. At this time, carbon dioxide was supplied to the autoclave at a rate of 0.315 l/min. Subsequently, the temperature was raised up to 178°C and the pressure inside the autoclave was increased to a gauge pressure of 5.0 atm by introducing carbon dioxide again. The contents were held for 2.0 hours to obtain 829.1 g of a reaction product. To this reaction product, 58.92 g of a 150 neutral oil was added as a diluent. This reaction product was transferred to a 1-liter three-necked pear type flask in an amount of 820.78 g and distilled off *in vacuo* to remove a small proportion of the ethylene glycol and most of the unreacted dodecylphenol to obtain 171.58 g of a distillation residue. In this distillation, the final distillation temperature was 225°C (3 mmHg). Thereafter, this distillation residue was diluted with a large amount of hexane and the resultant dilution was centrifuged to remove 2.15 g of insoluble matters. The hexane added in a large amount was then distilled off to obtain 167.09 g of a final product. Properties of the final product are shown. This final product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the resultant dilution was hydrolyzed at 93°C without adding a copper catalyst thereto by the same method as in the hydrolytic stability test method of ASTM D2619-88. The sample obtained after the 24-hour hydrolysis was centrifuged, and the base number of the resultant supernatant was measured. As a result, the base number retention after the hydrolysis was 95%.

#### EXAMPLE 2

[0055] The same procedure as in Example 1 was conducted, except that the addition amount of water was changed to 0.5 mol per mol of the calcium oxide. The yield of the final product was 164.39 g. Table 1 shows properties of the final product and the base number retention thereof after 24 hours, which was determined through a test in which the final product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the dilution was hydrolyzed without adding a copper catalyst thereto according to the hydrolytic stability test method of ASTM D2619-88.

#### EXAMPLE 3

[0056] The same procedure as in Example 1 was conducted, except that the addition amount of dodecylphenol was changed to 3.0 mol per ml of the calcium oxide, that of water was changed to 0.4 mol per mol of the calcium oxide, that of sulfur was changed to 0.2 mol per mol of the calcium oxide, and that of stearic acid was changed to 0.1 mol per mol of the calcium oxide. The yield of the final product was 163.68 g. Table 1 shows properties of the final product and the base number retention thereof after 24 hours, which was determined through a test in which the final product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the dilution was hydrolyzed without adding a copper catalyst thereto according to the hydrolytic stability test method of ASTM D2619-88.

#### EXAMPLE 4

[0057] The same procedure as in Example 1 was conducted, except that the pressure inside the reactor during the addition of ethylene glycol was changed to 200 kPa-G. The yield of the final product was 167.71 g. Table 1 shows prop-



erties of the final product and the base number retention thereof after 24 hours, which was determined through a test in which the final product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the dilution was hydrolyzed without adding a copper catalyst thereto according to the hydrolytic stability test method of ASTM D2619-88.

#### EXAMPLE 5

[0058] The same procedure as in Example 2 was conducted, except that the pressure inside the reactor during the addition of ethylene glycol was changed to 200 kPa-G. The yield of the final product was 166.01 g. Table 1 shows properties of the final product and the base number retention thereof after 24 hours, which was determined through a test in which the final product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the dilution was hydrolyzed without adding a copper catalyst thereto according to the hydrolytic stability test method of ASTM D2619-88.

#### EXAMPLE 6

[0059] The same procedure as in Example 1 was conducted, except that 0.46 mol of calcium stearate was used in place of 0.91 mol of stearic acid and that the amount of calcium oxide was changed to 1.44 mol. The yield of the final product was 165.91 g. Table 1 shows properties of the final product and the base number retention thereof after 24 hours, which was determined through a test in which the final product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the dilution was hydrolyzed without adding a copper catalyst thereto according to the hydrolytic stability test method of ASTM D2619-88.

#### COMPARATIVE EXAMPLE 1

[0060] The same procedure as in Example 3 was conducted, except that the pressure inside the reactor during the addition of ethylene glycol was changed to 300 kPa-G. The yield of the final product was 165.61 g. Table 1 shows properties of the final product and the base number retention thereof after 24 hours, which was determined through a test in which the final product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the dilution was hydrolyzed without adding a copper catalyst thereto according to the hydrolytic stability test method of ASTM D2619-88.

#### COMPARATIVE EXAMPLE 2

[0061] Properties of two commercial products of calcium phenate type additives which are generally on the market are shown in Table 1 together with the retentions of base number thereof after 24 hours, which were determined through a test in which each product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the dilution was hydrolyzed without adding a copper catalyst thereto according to the hydrolytic stability test method of ASTM D2619-88.

#### COMPARATIVE EXAMPLE 3

[0062] The same procedure as in Example 3 was conducted, except that the pressure inside the reactor during the addition of ethylene glycol was changed to 0 kPa-G. During the addition of ethylene glycol, nitrogen gas was passed at a rate of 10 ml/min in order to prevent air inflow. The discharge gas was ascertained to contain water vapor, which was thought to be the water yielded by the reaction. The yield of the final product was 163.32 g. Table 1 shows properties of the final product and the base number retention thereof after 24 hours, which was determined through a test in which the final product was diluted with an SAE No. 40 lubricating base oil to a base number of 30 mg-KOH/g and the dilution was hydrolyzed without adding a copper catalyst thereto according to the hydrolytic stability test method of ASTM D2619-88.

TABLE 1

	Base number (mg-KOH/g)	Viscosity (cSt/100°C)	Base number retention after hydrolysis (%)
Example 1	427	438	95

TABLE 1 (continued)

	Base number (mg-KOH/g)	Viscosity (cSt/100°C)	Base number retention after hydrolysis (%)
Example 2	444	390	98
Example 3	353	399	96
Example 4	396	560	93
Example 5	399	545	92
Example 6	431	461	95
Comparative Example 1	334	588	56
Comparative Example 2 (Commercial Product A)	250	300	33
Comparative Example 2 (Commercial Product B)	370	250	38
Comparative Example 3	310	350	61

## EXAMPLE 7

[0063] The concentrated product obtained in Example 1 (overbased alkaline earth metal phenate sulfide concentrate; base number: 427 mg-KOH/g; viscosity at 100°C: 438 cSt) was treated by the rubber film extraction method for 15 hours to obtain a light-brown solid (an overbased alkaline earth metal phenate sulfide) as a distillation residue. This residue had a base number of 576 mg-KOH/g. The distillation residue was diluted with a base oil purified by solvent dewaxing (aromatic content: 3.2 wt%) to a base number of 30, and the resultant dilution was evaluated for cleanness at 300°C using a hot-tube tester (HT-201 Type, manufactured by Komatsu Setsubi K.K.). As a result, the score thereof was 6.0.

## EXAMPLE 8

[0064] The concentrated product obtained in Example 2 (overbased alkaline earth metal phenate sulfide concentrate; base number: 444 mg-KOH/g; viscosity at 100°C: 390 cSt) was treated by the rubber film extraction method for 15 hours to obtain a light-brown solid as a distillation residue. This residue had a base number of 617 mg-KOH/g. The distillation residue was diluted with the same base oil as in Example 7 to a base number of 30, and the resultant dilution was evaluated for cleanness at 300°C using a hot-tube tester (HT-201 Type, manufactured by Komatsu Setsubi K.K.). As a result, the score thereof was 6.0.

## COMPARATIVE EXAMPLE 4

[0065] The same procedure as in Example 7 was conducted, except that a highly hydrogenated, purified base oil (aromatic content: 0.6 wt%) was used as a diluent oil. The cleanness of the resultant dilution was evaluated with the hot-tube tester and the cleanness score thereof was 4.5.

## EXAMPLE 9

[0066] The same procedure as in Example 7 was conducted, except that a 1:1 mixture of a highly hydrogenated, purified base oil (aromatic content: 0.6 wt%) and a base oil purified by solvent dewaxing (aromatic content: 3.2 wt%) was used as a diluent oil. The cleanness of the resultant dilution was evaluated with the hot-tube tester and the cleanness score thereof was 6.5.

## EXAMPLE 10

[0067] The same procedure as in Example 7 was conducted, except that a 1:1 mixture of a synthetic base oil containing no aromatics and a base oil purified by solvent dewaxing (aromatic content: 3.2 wt%) was used as a diluent oil. The cleanness of the resultant dilution was evaluated with the hot-tube tester and the cleanness score thereof was 6.0.

## EXAMPLE 11

[0068] The concentrated product obtained in Example 1 was diluted as it was with a base oil purified by solvent dewaxing (aromatic content: 3.2 wt%) to a base number of 30. The resultant dilution was evaluated for cleanness at 300°C using a hot-tube tester (HT-201 Type, manufactured by Komatsu Setsubi K.K.). As a result, the score thereof was 6.0.

## COMPARATIVE EXAMPLE 5

[0069] A commercial overbased calcium phenate sulfide type additive having a base number of 250 mg-KOH/g (Commercial Product A in Comparative Example 2) was treated by the rubber film extraction method in the same manner as for the concentrated product used in Example 7. The light-brown solid thus obtained as an extraction residue had a base number of 465 mg-KOH/g. This extraction residue was subjected to the hot-tube test in the same manner as in Example 1. As a result, the score thereof was 4.5.

## COMPARATIVE EXAMPLE 6

[0070] The same procedure as in Example 7 was conducted, except that a synthetic base oil containing no aromatic compound was used as a diluent oil. The cleanness of the resultant dilution was evaluated by the hot-tube tester and the cleanness score thereof was 5.0.

## INDUSTRIAL APPLICABILITY

[0071] The overbased alkaline earth metal phenate sulfide concentrate of the present invention can be used as detergent dispersants for lubricating oils or fuel oils or as alkaline detergents. The lubricating oils to which the concentrate is applicable are not particularly limited, and examples thereof include marine engine lubricating oils, generator engine lubricating oils, and hydraulic oils. The fuel oils to which the concentrate is applicable are also not particularly limited, and examples thereof include heavy oils for boilers. The amount of the overbased alkaline earth metal phenate sulfide concentrate to be added to lubricating or fuel oils is not limited. However, in engine oils for ships having a base number of about 30 mg-KOH/g, the addition amount thereof is generally from 1 to 10% by weight, preferably from 3 to 10% by weight.

## Claims

1. An overbased alkaline earth metal phenate sulfide concentrate having a base number of from 350 to 500 mg-KOH/g, a viscosity at 100°C of 1,000 cSt or less, and a fatty acid content of from 1 to 20% by weight based on the whole concentrate, wherein when the concentrate is diluted with an SAE No. 40 lubricating oil to a base number of 30 mg-KOH/g and the resultant dilution is hydrolyzed without adding a copper catalyst thereto by operation similar to the hydrolytic stability test method of ASTM D2619-88, a supernatant oil obtained by centrifuging the sample after 24 hours has a base number retention of 70% or more.
2. A process for producing the overbased alkaline earth metal phenate sulfide concentrate according to claim 1, comprising introducing an alkaline earth metal oxide, an alkaline earth metal hydroxide or a mixture thereof (hereinafter referred to as an "alkaline earth metal reagent"), a phenol compound in an amount of from 1 to 100 equivalents per mol of the alkaline earth metal reagent, and sulfur into a reactor optionally together with water; adding a dihydric alcohol to the introduced mixture at a pressure inside the reactor of 10 to 250 kPa-G to react them; subsequently distilling off the excess dihydric alcohol and at least the excess amount of the water; treating the resultant bottom residue with carbon dioxide in the presence of from 0.3 to 0.8 mol of water per mol of the alkaline earth metal reagent; causing from 0.001 to 0.3 mol of a fatty acid compound to be present per mol of the alkaline earth metal reagent before the carbon dioxide treatment at the latest; and distilling off the excess phenol compound contained in the product of the carbon dioxide treatment.
3. A lubricating oil composition having a base number of from 10 to 200 mg-KOH/g, comprising: an overbased alkaline earth metal phenate sulfide having a base number of from 550 to 700 mg-KOH/g and, when converted to an over-based alkali metal phenate concentrate having a base number of from 350 to 500 mg-KOH/g, shows the properties described in claim 1; and a lubricating base oil having a content of aromatic ingredients of from 1 to 10% by weight.
4. The lubricating oil composition of claim 3, which comprises a fatty acid having from 16 to 24 carbon atoms or a salt

thereof as a constitution component.

5. The lubricating oil composition of claim 3 or 4, which has a cleanness score of 5.5 or more according to a hot-tube test.

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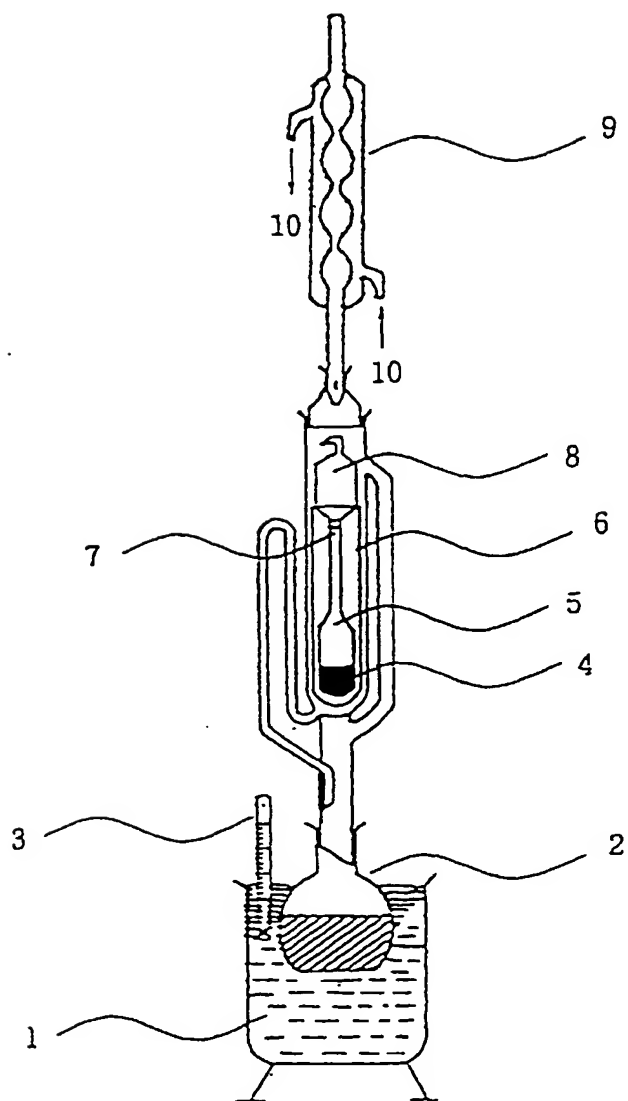
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FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/02012

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl. <sup>6</sup> C10M159/22, 169/04 // (C10M169/04, 101:02, 159:22), C10N10:04, 20:00, 20:02, 30:00, 30:04, 40:25, 70:00 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>6</sup> C10M159/22  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI (DIALOG)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, 95/25155, A1 (CHEVRON CHEMICAL S.A.), September 21, 1995 (21. 09. 95), Claims 1, 9 ; page 27, lines 5 to 17 ; Tables 1 to 3 & FR, 2717491, A1 & EP, 750659, A1 & EP, 786448, A2 & JP, 9-512287, A	1, 3
A	JP, 7-113095, A (Cosmo Research Institute, et al.), May 2, 1995 (02. 05. 95), Claim 1 & EP, 640682, A1 & US, 5446202, A & TW, 277057, A & CN, 1106383, A	1-5
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search July 16, 1998 (16. 07. 98)		Date of mailing of the international search report July 28, 1998 (28. 07. 98)
Name and mailing address of the ISA/ Japanese Patent Office  Facsimile No.		Authorized officer  Telephone No.

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